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(56) Documents Cited

GB 1547421 A

GB 1424378 A

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US 4503092 A

(58) Field of Search

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INT CL⁶ C09C 1/30 3/12

ON LINE: WPI

(54) Method for rendering inorganic powder hydrophobic

(57) Inorganic powder, preferably fumed silica, which has -OH groups attached to its surface, is rendered hydrophobic by mechanically fluidizing the raw inorganic powder with a silylating agent, where the silylating agent has a boiling point lower than the fluidizing temperature. The process can be either continuous or batch. A preferred silylating agent is a silazane eg hexamethyl disilazane.

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METHOD FOR RENDERING INORGANIC POWDER HYDROPHOBIC

Background of the Invention

The present invention relates to a method for treating inorganic powder with silylating agents in a batch or continuous manner, whereby the resulting inorganic powder is hydrophobic.

Inorganic powders, such as fumed silica, are used as thickeners, thixotropics, and reinforcing agents in materials such as inks, resins, rubber, paints and cosmetics. More particularly, they are used to modify the properties, such as the physical, mechanical and thermal properties, of a variety of plastic and elastomeric products such as room temperature vulcanizing silicone rubber, heat cured silicone rubber and liquid injection moldable silicone rubber.

Inorganic powders are also used as sorbents as disclosed in US Patent 5,037,557. For example, inorganic powders can be used to absorb hydrocarbons, such as oil, from water.

Untreated raw inorganic powder can have -OH groups on its surface that make it hydrophilic. To be effective as a filler or a sorbent, the inorganic powder must be rendered hydrophobic. A method typical of the prior art is disclosed in US Patent 4,554,147. This procedure involves a pneumatically fluidized bed process that requires the use of a quantity in excess of stoichiometric amounts of treating agent, such as a cyclic siloxane, long residence times and high operating temperatures. The operating conditions of the prior art processes make treated hydrophobic inorganic powder very expensive. For example, treated fumed silica is one of the most expensive ingredients incorporated in silicone rubber products.

An economically desirable process for hydrophobizing inorganic powder would be one that operates at moderate

temperatures with short residence times while using near stoichiometric amounts of treating agents. The present invention provides such a process.

The treated inorganic powder that results from the method of the instant invention can be substituted in applications that incorporate hydrophobic inorganic powders prepared by methods of the prior art. When the treated inorganic powder resulting from the method of the instant invention is incorporated into a final product, such as silicone rubber, properties of the final product, including physical, thermal and mechanical properties, are substantially unchanged from product that incorporates inorganic powder treated with methods of the prior art.

Summary of the Invention

In accordance with the present invention, there is provided a method for treating inorganic powder comprising mechanically fluidizing a raw inorganic powder in a silylating agent having a boiling point lower than the fluidizing temperature.

Detailed Description of the Invention

The present invention relates to a process for rendering raw inorganic powder hydrophobic by mechanically fluidizing the hydrophilic raw inorganic powder in a silylating agent.

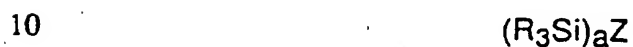
Raw inorganic powder can comprise any untreated inorganic material with -OH groups on its surface. Such raw inorganic powders and their methods of manufacture are well-known in the art. They include materials such as silica, powdered glass, silicates, alumina, titania, aluminum, asbestos, barium sulfate, zinc oxide, ferric oxide, zinc sulfide, and silver chloride. Preferably, the raw inorganic powder comprises amorphous silica, which includes

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fused and non-fused silica. More preferably, it comprises fumed silica with 50 - 450 m²/g surface area and 0.1 - 1% by weight moisture content.

5 Silylating agents are well known in the art. For use in the instant invention, the silylating agent must have a boiling point lower than the temperature at which the raw inorganic powder is being processed.

Suitable silylating agents include materials represented by the formula



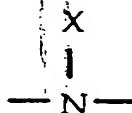
where each R is individually selected from the group consisting of mononuclear aryl radicals such as phenyl, tolyl, xylyl, and naphthyl; halogenated mononuclear and binuclear aryl radicals such as chlorophenyl and chloronaphthyl; mononuclear aryl lower
15 alkyl radicals having from 1 to 8 carbon atoms per alkyl group such as benzyl and phenylethyl; lower alkyl radicals having from 1 to 8 carbon atoms such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl and octyl; lower alkenyl radicals having from 2 to 8 carbon atoms such as vinyl, allyl and 1-propenyl; halo lower alkyl radicals having from 1 to 8
20 carbon atoms such as chloropropyl and trifluoropropyl; cycloalkyl radicals such as cyclobutyl, cyclopentyl and cyclohexyl;

where a is an integer equal to 1 or 2; and,

where Z is a radical selected from -OH, -NR'X, -ONR'2, -SR', -O-, -S-,



and



where R' is selected from the group consisting of H and R, where R is as above defined; where X is selected from the group consisting of H and R. R' is preferably H, lower alkyl or cycloalkyl and X is preferably H, lower alkyl or cycloalkyl.

Silylating agents which can be employed in the instant invention are illustrated by triorganosilylmercaptans; triorganosilylacylates; triorganosilylamines such as trimethylsilylisopropylamine, trimethylsilylamine, dimethylphenylsilylamine and dimethylvinylsilylamine; triorganosilylaminoxy compounds such as diethylaminoxytrimethylsilane and diethylaminoxydimethylphenylsilane. There also can be employed disilyl compounds including disiloxanes such as hexamethyldisiloxane, 1,1,3-divinyldimethyltetramethyldisiloxane and 1,3-diphenyldimethyltetramethyldisiloxane; and silazanes such as hexamethyldisilazane and 1,3-diphenylhexamethyldisilazane. The preferred silylating agents are the triorganosilylamines and the silazanes.

More preferably, the silylating agent comprises trimethyl silylating agents, such as hexamethyldisilazane, trimethylsilanol and bis(trimethylsilyl)carbonate.

The amount of silylating agent used in the method determines in part the degree of surface -OH removal. An -OH group

is considered removed when an active hydrogen from an organic molecule is displaced by a silyl group represented by the formula $-\text{SiR}_3$, where R is as previously defined. For example, an $-\text{OH}$ group is considered removed when the hydrogen is replaced by $-\text{Si}(\text{CH}_3)_3$.

- 5 The more silylating agent utilized, the more surface $-\text{OH}$ removal occurs. Preferably, an amount of silylating agent is utilized that is near a stoichiometric quantity based on the amount of surface $-\text{OH}$. The appropriate amount is determinable by those skilled in the art.

- 10 The raw inorganic powder and the silylating agent are mechanically fluidized. The fluidizing can be accomplished by any equipment known in the art which will provide thorough blending and constant mechanical agitation sufficient to suspend the raw inorganic powder particles in the volatilized silylating agent. The fluidizing can be conducted as a batch process or as a continuous process.
- 15 Suitable fluidizing equipment comprises mixers which incorporate rotating impellers with various blade angles, kneading-type mixers, helical-blade mixers, and screw mixers.

- During the fluidizing, the process temperature must be maintained above the boiling point of the silylating agent. Preferably, the temperature is maintained below 300°C . More preferably, it is held between $140 - 240^\circ\text{C}$.
- 20

- Reaction time is dependent on the degree of fluidizing and the fluidizing temperature. It is also dependent on the amount of surface $-\text{OH}$ removal that is desired. The longer the reaction is allowed to proceed, the greater the amount of surface $-\text{OH}$ that will be removed from the inorganic powder. With a higher fluidizing temperature, a shorter reaction time is required to achieve a desired level of $-\text{OH}$ removal. The necessary level of $-\text{OH}$ removal and the time and temperature parameters required to meet that level will be determinable by those skilled in the art.
- 25
- 30

The excess reagents and by-products can be stripped from the treated inorganic powder by any method. Suitable stripping methods are well known in the art. They include displacing the excess reagents and by-products with nitrogen. Preferably, the excess reagents and by-products are stripped by applying dynamic vacuum at the same temperature as the process temperature and breaking the vacuum in nitrogen.

Example 1

900 g of raw untreated fumed silica containing approximately 0.4% moisture with approximately 4.5 OH/nm² was fluidized in a 10 liter Drais® mixer with 8% by weight hexamethyldisilazane, which is 2% over the stoichiometric amount of 6% by weight hexamethyldisilazane, for 7 minutes at 160°C. The excess reagents and by-products were stripped from the treated fumed silica by applying dynamic vacuum for 10 minutes at 160°C and breaking the vacuum in nitrogen. The degree of -OH removal was determined by three techniques: ²⁹Si NMR, FTIR and carbon analysis. All of the isolated -OH groups, comprising approximately 1.4 - 1.5 surface OH/nm², were removed.

Example 2 (Control)

900 g of raw untreated fumed silica containing approximately 0.4% moisture with approximately 4.5 OH/nm² was treated with mixed cyclics (D_x, x = 3 - 6) in a batch reactor that was mechanically mixed but not fluidized for 4 hours at 270°C. The excess reagents were stripped from the treated fumed silica by using a stream of nitrogen. The degree of -OH removal was determined by three techniques: ²⁹Si NMR, FTIR and carbon analysis. All of the isolated -OH groups, comprising approximately 1.4 - 1.5 surface OH/nm², were removed.

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The same level of -OH removal was obtained in Example 2 as in Example 1. However, the total reaction time was much longer: Example 2 took 4 hours compared to 7 minutes in Example 1, and the reaction temperature was considerably higher: in
5 Example 2 the temperature was 270°C compared to 160°C in Example 1.

Example 3

180 g of raw untreated fumed silica containing approximately 0.4% moisture with approximately 4.5 OH/nm² was
10 fluidized in a 3.8 liter laboratory mixer with 20% by weight hexamethyldisilazane for 40 minutes at 180°C. The excess reagents and by-products were stripped from the treated fumed silica by applying dynamic vacuum for 10 minutes at 180°C and breaking the vacuum in nitrogen. The degree of -OH removal was determined by
15 three techniques: ²⁹Si NMR, FTIR and carbon analysis. Approximately 2.0 - 2.2 surface OH/nm² was removed.

Example 4 (Control)

180 g of raw untreated fumed silica containing approximately 0.4% moisture with approximately 4.5 OH/nm² was
20 treated with mixed cyclics (D_x, x = 3 - 6) in a batch reactor that was mechanically mixed but not fluidized for 4 hours at 270°C. It was subsequently treated in a batch reactor that was mechanically mixed but not fluidized with 16% by weight hexamethyldisilazane for 12 hours at 180°C. The excess reagents were stripped from the treated
25 fumed silica by using a stream of nitrogen. The degree of -OH removal was determined by three techniques: ²⁹Si NMR, FTIR and carbon analysis. Approximately 2.0 - 2.2 surface OH/nm² was removed.

The same level of -OH removal was obtained in
30 Example 4 where as in Example 3. However, the total reaction time

was much longer: Example 4 took 16 hours compared to 40 minutes in Example 3.

Example 5

5 The properties of silicone rubber which incorporates the treated fumed silica of the instant invention remain substantially unchanged from those of the silicone rubber which incorporates the treated fumed silica of the prior art.

10 Polydimethylsiloxane gum was compounded with the fumed silica generated in each of Examples 1 through 4. Shore A hardness and % Elongation were tested using the method of ASTM D412-87. Die C tear strength was tested using the method of ASTM D624-86. The test results tabulated below indicate that the method of treating the fumed silica does not substantially affect the resulting rubber's properties.

15	Sample	Shore A	Die C (kN/m)	% Elongation
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20	Example 1	28	94	839
	Example 2(Control)	27	95	782
	Example 3	24	76	860
	Example 4(Control)	23	72	860

25 Example 6

The treated filler of examples 1 and 2 were also formulated into high durometer SE6075® silicone rubber, a product of General Electric Silicones, Waterford, NY. Shore A hardness, modulus, tensile strength and % elongation were tested per ASTM
30 method D412-87. Die B tear strength was tested per ASTM D624-86.

The following table details the physical properties of both filled systems.

- 5 The properties of the high durometer silicone rubber which incorporates the treated fumed silica of the instant invention remained substantially unchanged from those of the high durometer silicone rubber which incorporates the treated fumed silica of the prior art.

	Example 1	Example 2 (control)		Example 1	Example 2 (control)
Curing Method	Peroxide-Cured	Peroxide-Cured		Pt-Cured	Pt-Cured
Shore A	74	74		64	65
Die B	136	133		304	300
100% Modulus	401	373		241	251
%Elongat.	379	408		949	920
Tensile	1464	1427		1287	1295

CLAIMS:

1. A method for treating raw inorganic powder comprising mechanically fluidizing a raw inorganic powder and at least one silylating agent having a boiling point lower than the fluidizing temperature.

2. A method in accordance with Claim 1, wherein said raw inorganic powder is selected from the group consisting of silica, powdered glass, silicates, alumina, titania, aluminum, asbestos, graphite, carbon black, barium sulfate, zinc oxide, ferric oxide, zinc sulfide, and silver chloride.

3. A method in accordance with Claim 1, wherein said raw inorganic powder comprises fumed silica.

4. A method in accordance with Claim 1, wherein said silylating agent comprises the formula

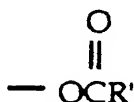


where each R is individually selected from the group consisting of mononuclear aryl radicals; halogenated mononuclear and binuclear aryl radicals; mononuclear aryl lower alkyl radicals having from 1 to 8 carbon atoms per alkyl group; lower alkyl radicals having from 1 to 8 carbon atoms; lower alkenyl radicals having from 2 to 8 carbon atoms; halo lower alkyl radicals having from 1 to 8 carbon atoms; cycloalkyl radicals;

where a is an integer equal to 1 or 2; and,

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where Z is a radical selected from the group consisting of -OH, -NR'¹X, -ONR'², -SR', -O-, -S-,



15 where R' is selected from the group consisting of H and R and where X is selected from the group consisting of H and R.

5. A method in accordance with Claim 4 wherein said R' is selected from the group consisting of H, lower alkyl and cycloalkyl.

6. A method in accordance with Claim 4 wherein said X is selected from the group consisting of H, lower alkyl and cycloalkyl.

7. A method in accordance with Claim 1, wherein said silylating agent is selected from the group consisting of triorganosilylmercaptans, triorganosilylacrylates, triorganosilylamines, triorganosilylaminoxy compounds, disilyl compounds and
5 triorganosilylamines.

8. A method in accordance with Claim 1, wherein said silylating agent comprises a silazane.

9. A method in accordance with Claim 1, wherein said silylating agent comprises a trimethyl silylating agent.

10. A method in accordance with claim 1, wherein said fluidizing is performed at a temperature below 300°C.



The
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Office

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Application No: GB 9611094.5
Claims searched: 1-10

Examiner: C.A. Clarke
Date of search: 24 July 1996

Patents Act 1977
Amended Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:
UK CI (Ed.O): C1A (APC, APF4, AVF1)
Int CI (Ed.6): C09C 3/12, 1/30
Other: WPI

Documents considered to be relevant:

Category	Identity of document and relevant passage		Relevant to claims
X	GB1547421	DEUTSCHE GOLD-UND-SILBER see whole document	1-3 and 10 at least
X	GB1424378	DEUTSCHE GOLD-UND-SILBER see claims 14-15	1-3 at least
Y	GB 1024234	MIDLAND SILICONES see p2 lines 83-85 and claim 7	2-6,8-10
X	US 4503092	DEGUSSA see claim 1	1-3 at least

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.



Application No: GB 9611094.5
Claims searched: 1-10

Examiner: C.A. Clarke
Date of search: 22 July 1996

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections including GB, EP, WO & US patent specifications, in:
UK CI (Ed.O): C1A (APC, APF4, AVF1)
Int CI (Ed.6): C09C 3/12, 1/30
Other: WPI

Documents considered to be relevant:

Category	Identity of document and relevant passage		Relevant to claims
X	GB1547421	DEUTSCHE GOLD-UND-SILBER see whole document	1-3 and 10 at least
X	GB1424378	DEUTSCHE GOLD-UND-SILBER see claims 14-15	1-3 at least
Y	GB 1024324	MIDLAND SILICONES see p2 lines 83-85 and claim 7	2-6,8-10
X	US 4503092	DEGUSSA see claim 1	1-3 at least

X Document indicating lack of novelty or inventive step
Y Document indicating lack of inventive step if combined with one or more other documents of same category.

& Member of the same patent family

A Document indicating technological background and/or state of the art.
P Document published on or after the declared priority date but before the filing date of this invention.
E Patent document published on or after, but with priority date earlier than, the filing date of this application.

